METHOD FOR PREPARING MANGANESE-BASED NITRIDE HAVING NEARLY ZERO TEMPERATURE COEFFICIENT OF RESISTIVITY

BACKGROUN OF THE INVENTION

Field of the Invention

The present invention relates to a method for preparing manganese-based nitride having nearly zero temperature coefficient of resistivity and more particularly, to the effective method for preparing manganese-based nitride expressed by the formula (1), wherein the manganese-based nitride, prepared by heating the stoichiometric mixture of Mn_2N and Cu in an evacuated quartz tube, provides some advantages in that i) the use of the Mn_2N compound as a reactant, the formation of impurities and nitrogen evaporation can be prevented, and ii) through nitrogen is tightly bonded between metals, the manganese-based nitride has extremely low (46 ppm/K) temperature coefficient of resistivity and a cubic antiperovskite structure.

$CuNMn_3$ (1)

Temperature coefficient of resistivity (TCR) is an index of the changes of resistance with temperature and is determined by measuring the incremental change in resistance of a resistive material with temperature change, $(1/R_0) \times (dR/dT)$, where R_0 is the initial resistance. When the TCR value is close to that of zero TCR material is typically less than 25 ppm/K, the resistance change is less than 0.25% with 100℃ of temperature difference.

Such materials having nearly zero TCR are widely used in the field of precision measurement and thin film resistor. Manganin, which is widely

used as cryogenic resistor at very low temperature of 10 K, is an alloy comprised 84wt.% of copper, 12wt.% of Manganese-based and 4wt.% of Nickel and used the most in precision measurement resistor. Manganin has about 20 ppm/K of resistance change with 10℃ of temperature difference.

However, this alloy film possesses intrinsic problems of rapid increase in surface resistance due to oxidation on metal surface and poor adhesion due to large structural strain.

SUMMARY OF THE INVENTION

As a result of intensive studies to develop the compound having low temperature coefficient of resistivity, low structural strain and stable in air, the inventors have completed by providing stable $CuNMn_3$ in air having a cubic antiperovskite structure.

An object of the invention is to provide a preparing method of manganese-based nitride having nearly zero temperature coefficient of resistivity which has more stability in air and higher adhesion then the metal alloy.

Brief Description of the Drawings

Fig. 1 is a graph showing X-ray powder diffraction patterns of $CuNMn_3$ according to the present invention.

Fig. 2 is a graph showing the temperature dependent magnetization of $CuNMn_3$ according to the present invention.

Fig. 3 is a curve showing the temperature dependent resistance with no magnetic field of $CuNMn_3$ according to the present invention.

Fig. 4 is a curve showing the resistance change at a temperature from 250K to 350K of $CuNMn_3$ according to the present invention.

Detailed Description of the Invention

The present invention is characterized by a method for preparing manganese-based nitride having a cubic antiperovskite structure, wherein the stoichiometric mixture of Mn_2N and Cu is sintered at 800-900℃ for 40-60 hrs in an evacuated quartz tube to produce a manganese-based nitride expressed by the following formula (1).

$$CuNMn_3 \qquad (1)$$

The present invention is described in detail as set forth hereunder.

Reactants of the present invention are Mn_2N and copper (Cu). The use of Mn_2N compound promotes the formation of materials having desired antiperovskite structure and stability in air because nitrogen is tightly sorrounded between metals and thus, it cannot evaporate easily. And further, the use of Mn_2N compound prevents from contamination of impurities. Amount of Mn_2N is used in the molar ratio of 1.45-1.55 mole per mole of copper. If it deviated the molar ratio range of 1.45-1.55, the temperature coefficient of resistivity rapidly increase and the antiperovskite structure is not formed, respectively. The reaction of Mn_2N and Cu is expressed in the following reaction formula 1.

Reaction Formula 1

$$1.5Mn_2N + Cu \Rightarrow CuNMn_3$$

The preparing method of manganese-based nitride of the present invention is described in more detail hereunder.

All processes are carried in a dry box, being filled with argon gas so as to avoid any contact with air. A mixture of Mn_2N powder and Cu powder according to stoichiometric ratio as in reaction formula 1, is placed in a dry box, weighted, mixed, ground and molded in the form of pellet and wrapped with tantalum foil. The pellet is placed into a quartz tube under vacuum. The air in the quartz tube was evacuated for 30 min and sealed with a torch. With a slow increase of temperature up to 800-900℃, the pellet in the quartz tube is sintered at the same temperature for 40-60 hrs to obtain $CuNMn_3$ having a cubic antiperovskite structure. If the temperature is lower than 800℃, it is impossible to obtain a cubic antiperovskite structure of $CuNMn_3$. On the other hand, in case of exceeding the temperature of 900℃, the antiperovskite structure becomes decomposed slowly. And further, if the sintered time deviates from the above range, the desired Cu-Mn alloy is not generated.

The method of the present invention minimizes the contamination of impurities by using Mn_2N compound and provides excellent durability. The prepared $CuNMn_3$ is determined to have a cubic antiperovskite structure by X-ray powder diffractometer and 40-50 ppm/K of a temperature coefficient of resistivity and thus, it can be effectively utilized in thin film resistor due to excellent stability in air.

The following examples are intended to be illustrative for the present invention and should not be construed as limiting the scope of this invention defined by the appended claims.

Example 1 : Preparation of $CuNMn_3$

Mn_2N (1.50g) and Cu (0.513g) were placed in a dry box, weighted, mixed and molded in the form of pellet. The mixture was then wrapped with tantalum foil, placed into a quartz tube and sealed under vacuum after evacuating the quartz tube for 30 min with vacuum pump. After the quartz tube was placed in an electric furnace of which temperature was raised to 800-900℃ with a rate of 50℃/h, the pellet was sintered at the same temperature for 50 hr. Then, the temperature of pellet was slowly cooled and taken out from the quartz tube to produce a black pellet of $CuNMn_3$.

The structure of $CuNMn_3$ was determined to be a cubic structure with space group *Pm3m* and a lattice parameter of a=3.90465(9) Å as displayed in Fig. 1.

The magnetization data as a function of temperature for $CuNMn_3$ was shown in Fig. 2, revealing a paramagnetic to ferromagnetic transition near 150K.

Fig. 3 shows the resistivity curve for $CuNMn_3$. The resistivity continuously increased with temperature up to 150K, exhibiting typical metallic character. Above this temperature, on the other hand, the resistivity data appeared to be nearly independent of temperature. The resistivity characteristic was shown clearly in Fig. 4 which was for extended region between 250 K to 350 K.

Comparative Example 1

Mn instead of Mn_2N used in Example 1 and Cu (3:1) were mixed and

sintered under N_2. The Cu-Mn alloy was prepared in the same manner as in Example 1.

Comparative Example 2

A final product was prepared in the same manner as in Example 1 except for raising temperature with a rate of 200℃/h instead of 50℃/h. As a result, the compound having an antiperovskite structure was produced with impurity of Cu-Mn alloy.

Comparative Example 3

A final product was prepared in the same manner as in Example 1 except for skipping of wrapping with tantalum foil. As a result, the compound having an antiperovskite structure was produced with impurity of Cu-Mn alloy.

Experimental Example : Determination of temperature coefficient of resistivity

After resistivity value of $CuNMn_3$ prepared in Example 1 was measured by standard four-probe method, temperature coefficient of resistivity was obtained from the equation of (1/R0) X (dR/dT) in the temperature range of 250 K to 350 K. The result was summarized in Table 1. Thermal expansion coefficients and temperature coefficients of resistivity of pure Cu, Al and manganin were also summarized in Table 1.

Table 1

Category	Thermal expansion coefficient (1/K)	Temperature coefficient of resistivity (ppm/K)
Example 1	$1.77x10^{-5}$	46 at 300 K
Manganin	-	20 at 10 K
Copper (Cu)*	$1.68x10^{-5}$	4360 at 300 K
Aluminum (Al)*	$2.44x10^{-5}$	4430 at 300 K
* Obtained from literature		

As shown in Table 1, the manganese-based nitride prepared in Example 1 has lower temperature coefficient of resistivity than that of the conventional alloy in the wide range of room temperature. And further, the structure of manganese-based nitride of the present invention is much more stable in air compared to the conventional alloy because nitrogen is tightly bounded between metals.

The $CuNMn_3$ compound of the present invention having a cubic antiperovskite structure not only is thermally stable in air but also is difficult to be oxidized. Thus, the perovskite material can be useful in developing a wide range of hybrid materials combined with various perovskite oxides such as $Pb(Zr, Ti)O_3$(PZT).